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A CHEMICAL DETERMINATION OF DDT^{1/}

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In the absence of a specific color test for 2,2-bis(p-chlorophenyl)-1,1,1-trichloroethane, commonly known as DDT, the high chlorine content (50.01 percent) of this compound can be utilized as a basis for its indirect chemical analysis. Of the various known methods applied to DDT for chlorine analysis, we have found that the Carius method has given consistently accurate results. The Carius method, however, is not only time-consuming but also requires a painstaking technique if it is to be used without hazard. We have therefore modified a method proposed by Winter^{2/} for the determination of halogen in organic compounds. In principle the sample to be analyzed is volatilized and burned in a flame of ordinary illuminating gas, the chlorine-containing combustion products are absorbed in an alkaline solution of sodium arsenite, and this solution is then titrated for chloride ion, using standard solutions of silver nitrate and ammonium thiocyanate.

Apparatus

The apparatus (fig. 1) consists of a Pyrex glass tube, ABC, shaped in the form of a U, to one end of which is sealed a short length of 1.5-mm. capillary tubing. This U-tube is heated electrically by a winding of about 10 feet of nichrome resistance wire (No. 28 B. & S. gage) spaced at about 10 turns per inch. The nichrome wire, W, is held in place by a strip of braided asbestos tape, T, underlying the wire, and by 2 or 3 single loops, L, of wire made tight by twisting the ends together. The terminal leads of the nichrome wire are connected to a variable transformer (Variac), V. The chimney, D, is made from a short piece of 20-mm. Pyrex tubing joined to a piece of 9-mm. tubing. This is connected to the inlet, M, of the gas-washing bottle, G, by a short length of rubber tubing, F. The fritted glass disc, H, is covered by the absorbing solution, S. The outlet, K, of the gas-washing bottle is connected by rubber tubing, R, to a water aspirator (not shown). Only a moderate suction is needed to draw the combustion products from the chimney, through the absorbing solution. A pinch clamp, P, over the rubber tubing, R, is used to regulate the amount of suction.

^{1/} Some of the work reported was done under a transfer of funds recommended by the Committee on Medical Research from the Office of Scientific Research and Development to the Bureau of Entomology and Plant Quarantine.

^{2/} Winter, P. K. Determination of halogen in organic compounds. Indus. and Engin. Chem., Analyt. Ed. 15: 571-574. 1943.

Reagents and Solutions

Absorbing Solution.--Five grams of arsenic trioxide is dissolved in 100 ml. of a solution containing 8 grams of sodium hydroxide, and made up to 1 liter with distilled water.

Silver Nitrate Solution.--4.791 grams of silver nitrate is dissolved in distilled water and made up to 1 liter in a volumetric flask. This gives a calculated normality of 0.0282 so that 1 ml. of solution is equivalent to 1 mg. of chloride ion.

Ammonium Thiocyanate Solution.--2.147 grams of ammonium thiocyanate is dissolved in distilled water and made up to 1 liter in a volumetric flask. This is calculated for a normality of 0.0282 equivalent to that of the silver nitrate solution.

Other Reagents.--Powdered ferric sulfate, concentrated nitric acid (halogen-free), and nitrobenzene are also needed.

Procedure

A suitable aliquot of the silver nitrate solution is titrated with the ammonium thiocyanate solution, about 3 ml. of nitric acid added and 0.5 gram of ferric sulfate being used as the indicator. The strength of the thiocyanate solution must then be adjusted so that it is exactly equivalent to that of the silver nitrate solution; otherwise it becomes necessary to use a correction factor. The silver nitrate solution may be standardized directly against the combustion of a weighed amount of pure DDT or against the combustion of an aliquot of an accurately made-up solution or emulsion of known DDT concentration. The material for standardization should be of the same nature and form as the material being analyzed, i.e., whether a pure or technical grade of DDT, and whether it is in the form of a solution, emulsion, or dust.

With 50 ml. of the absorbing solution in the gas-washing bottle and with the apparatus connected up as shown, exactly 1.00 ml. of the solution or emulsion containing the DDT under determination is introduced by means of a 1-ml. precision-quality transfer pipette inserted through the opening A, into the B portion of the U-tube. The U-tube is then connected at A by means of rubber tubing (not shown) to an outlet of illuminating gas. Before the gas is turned on, the U-tube is lowered and removed from the chimney. With the Variac set at 15 volts, the gas is then ignited at the capillary opening, C, and the flame is adjusted to a height of about 15 cm. After 10 minutes, when the solvent carrying the DDT is largely burned, the height of the flame is reduced to about 1 cm. The U-tube is raised to insert the flame in the chimney, and by manipulating the pinch clamp, P, the suction from the water aspirator is adjusted so that sufficient air is drawn through the system to support the flame. During the course of about 45 minutes the heat input is gradually increased by raising the voltage from the Variac. A sooty flame should be avoided by increasing the heat gradually or having sufficient air drawn through the system. It will be observed that the flame becomes quite luminous as the DDT is volatilized. For the last 10 minutes the setting of the Variac should be about 100 volts. This setting should deliver current to impart a dull red glow to the nichrome wire.

The gas is then turned off, the inlet tube, M, removed from G, and adhering solution quantitatively rinsed with distilled water through the disk H by means of a wash bottle into container G. The solution in G is then quantitatively transferred to a 500-ml. Erlenmeyer flask. Likewise the chimney, after cooling, is rinsed with a little distilled water into the flask. Silver nitrate solution in excess of the amount necessary to precipitate all the chloride ion is added from a burette to the alkaline absorbing solution in the flask. There is then added in succession approximately 3 ml. of concentrated nitric acid, 0.5 gram of ferric sulfate, and 5 ml. of nitrobenzene. The flask is swirled to coagulate most of the precipitate. Then the excess of silver nitrate is back-titrated with the thiocyanate solution until a faint pink color appears. As recommended by Winter, it has been found preferable to cross-titrate with both standard solutions, crossing the end point in each direction. The end point, which is not too sharp, is more easily perceived in this way. Since the two standard solutions have been made exactly equivalent, no calculation is involved other than subtraction of the amount of thiocyanate solution used from the amount of silver nitrate solution to obtain the quantity of silver nitrate solution consumed. Each milliliter will be approximately equivalent to 2 mg. of DDT. The exact figure is determined, as previously mentioned, by standardization of the silver nitrate solution against the combustion of the DDT being used. The technical grade of DDT may contain 48 to 51 percent of chlorine. It may be assumed, however, that the chlorine content of a given batch of DDT is sufficiently uniform to justify the use of this method. Where the purified grade of DDT is used, the silver nitrate solution should of course be standardized against the purified DDT and not against the technical grade.

Determination of DDT in Emulsions

We first applied this method to the analysis of samples taken from large batches of an emulsion reported to contain 2 percent of technical DDT, used in the impregnation of clothing. To control this batch-processing operation it was necessary to check the percentage of DDT contained in the emulsion from time to time during the processing. A 5-percent emulsion was made up using a technical grade of DDT. A portion of this material was then diluted to a strength of 1 percent, and both samples were analyzed for chlorine content. Upon titration with silver nitrate solution, which had been standardized against constant-boiling hydrochloric acid, the results in both cases showed the chlorine content of the DDT to be 44 percent. Since these low results were found to be consistently reproducible, and on the assumption that technical DDT contains 50 percent of chlorine, a correction factor was introduced to give the results in percentage of technical DDT.

Table 1 shows the calculation of this correction factor. Table 2 gives the results obtained in the control analyses on 2-percent emulsions used for impregnating clothing. The use of a correction factor is obviated by the standardization of the silver nitrate solution against the combustion of the DDT being used as already recommended under Procedure. The titer is then expressed directly in milligrams of DDT rather than in milligrams of chloride ion per milliliter of silver nitrate solution.

Application of Method to Spray Deposits or Residues

In determinations of spray deposits or residues of DDT on plants^{3/}, the plant material may be extracted with a suitable solvent such as xylene, cyclohexanone, or benzene, and made up to a definite volume. A 1-ml. aliquot of this extract can be run by this method in precisely the same way as described for the DDT emulsions. Where only minute amounts of DDT are encountered, sufficient plant material should be extracted or the extract should be concentrated by evaporation of solvent, so that a 1-ml. aliquot contains a minimum of 1 mg. and preferably about 50 mg. of DDT. In case the DDT concentration in the solvent is very low, several 1- or 2-ml. aliquots may be concentrated successively in the combustion tube, with the Variac set at 15 volts. The aspirator is then adjusted and the combustion carried out.

It should, of course, be borne in mind that the presence of other halogen-containing compounds may interfere with the determination of DDT by this method.

Summary

A modification of Winter's method for the determination of halogen in organic compounds has been adapted to the determination of DDT. About 1 hour is required for an analysis to be carried out, and the method is sufficiently sensitive for the determination of DDT in spray residues.

^{3/} Fahey, J. E. The Determination of DDT Spray Deposits on Apples. Submitted for publication.

Table 1.--Analyses of DDT emulsions, showing calculation of the correction factor

Concentration of DDT in sample	Amount of sample	Chlorine		DDT	
		Calcd.	Found	Calcd.	Found
Percent (wt./vol.)	Ml.	Mg.	Mg.	Mg.	Mg.
5	1.00	25.0	21.7	50.0	43.4
	1.00	25.0	21.9	50.0	43.8
	1.00	25.0	22.1	50.0	44.2
	Av.	25.0	22.0	50.0	44.0
	2.00	50.0	44.2	100.0	88.4
1	1.00	5.0	4.4	10.0	8.8
	1.00	5.0	4.4	10.0	8.8
	Av.	5.0	4.4	10.0	8.8
0 (blank)	1.00	0.0	0.0	0.0	0.0

Correction factors: For 5-percent emulsion, $50.0/44.0 = 1.14$;
for 1 percent emulsion, $10.0/8.8 = 1.14$.

Table 2.--Control analyses on 2-percent DDT emulsions used for impregnating clothing

Description of sample	Chlorine		DDT (cor. value)	
	Found	Cor. value		
	Mg.	Mg.	Mg.	Percent (wt./vol.)
Dipping solution (1-ml. samples):				
Before dipping of first batch	8.6	9.8	19.6	1.96
End of first batch	8.1	9.2	18.4	1.84
End of second batch	8.4	9.5	19.0	1.90
End of tenth batch	6.9	7.8	15.6	1.56
First sample on following morning	7.9	9.0	18.0	1.80
New lot before dipping	8.9	10.1	20.2	2.02
End of tenth batch	8.5	9.7	19.4	1.94
Concentrate ^{1/} (0.3-ml. samples):				
Initial	26.2	29.8	59.6	19.9
Composite, drums 1 and 2	26.4	30.0	60.0	20.0
Composite, drums 3 and 4	25.7	29.2	58.4	19.5

^{1/} Containing 20 percent of DDT (technical grade) plus a wetting agent and an organic solvent.

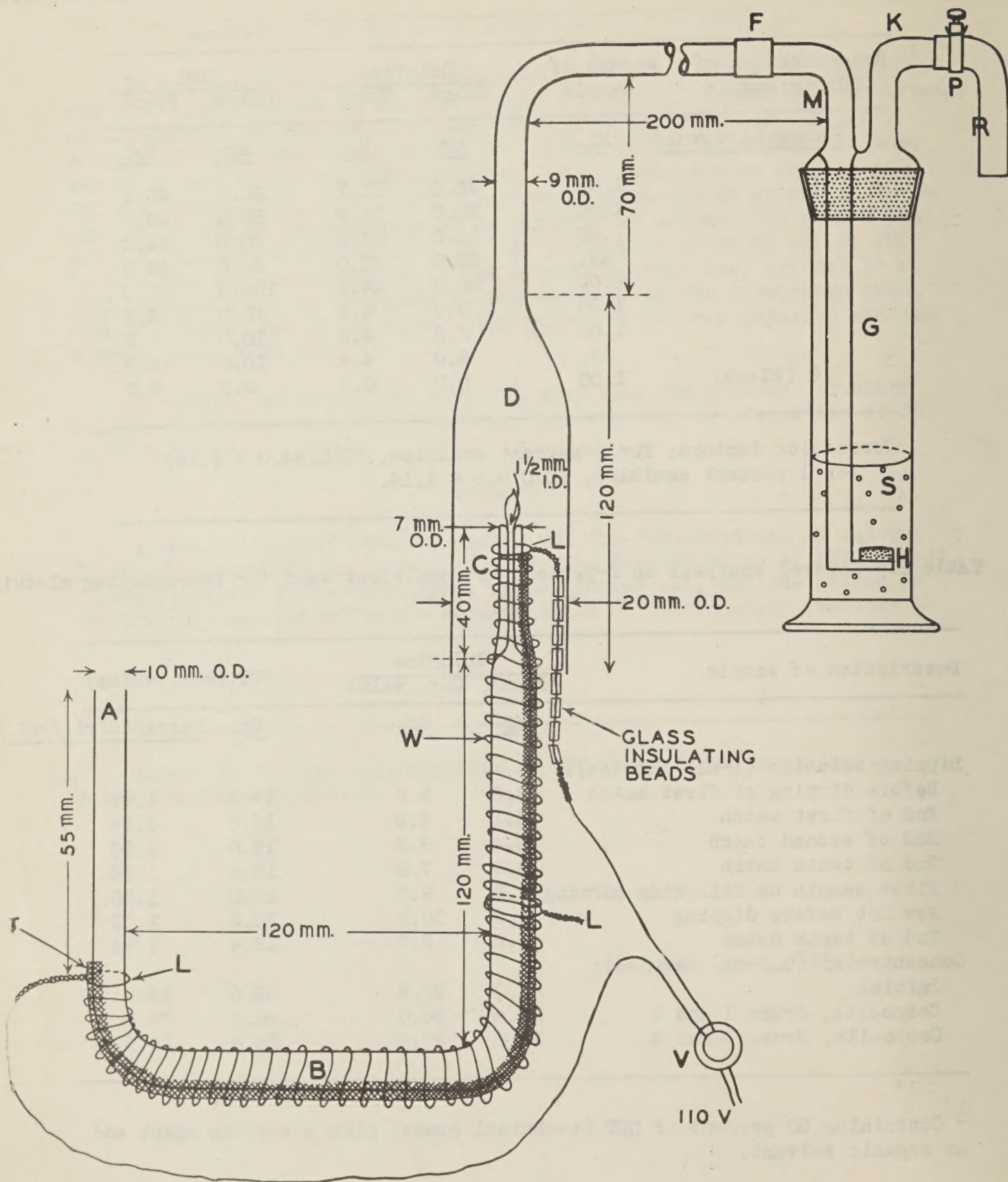


Figure 1.--Apparatus used for chemical determination of DDT.